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(54) Title: LASER MARKABLE MATERIAL

(57) **Abstract:** A laser markable material comprising a thermoplastic elastomer and a pigment additive, the pigment additive having an absorption band in a band of e.m. radiation which results in a photo-chemical reaction taking place when the material is subjected to e.m. radiation in the absorption band. A method of marking the laser markable material comprises subjecting the material to a laser beam having a wavelength of radiation in the absorption band such that the pigment undergoes a photo-chemical reaction.

LASER MARKABLE MATERIAL

This invention relates to material that is capable of being marked by a laser and in particular to laser-markable thermoplastic elastomer material.

Currently keymats for portable devices such as mobile phones are made of silicon rubber by a compression moulding process. Texts and graphics are then manually printed by a silk-screen printing process and manually inspected by operators. This conventional process has many disadvantages: the silicon rubber keymat cannot be recycled economically; the production cycle time is long (more than one hour); the process is labour intensive and difficult to automate; and the quality of the resulting component is inconsistent and heavily depends on human skills.

Laser marking technology is also widely used in industry because of its superior mark quality and flexibility to traditional marking techniques. Examples of such applications include laser marking on IC chips, aircraft cables and metal surfaces of various products.

However, the current technique of laser marking on polymers such as thermoplastic elastomer, polyethylene, polypropylene and polycarbonates is through a thermal process. The laser beam heats up the materials and causes melting and vaporisation of the surface material. Grooves are produced with re-solidified material particles. As articles such as keymats have high cosmetic requirements, the laser marking quality through thermal processes is not acceptable.

Infrared lasers such as CO2 and Nd:YAG lasers produce colour changes through thermal processes, which result in material melting and vaporisation.

According to the invention there is provided a material comprising a thermoplastic elastomer and a pigment additive, the pigment additive having an absorption band in a band of e.m. radiation which results in a photo-chemical reaction taking place when the material is subjected to e.m. radiation in the absorption band.

The invention results in a material which may be subjected to laser marking by photo-chemical transformation rather than thermal changes. The photo-chemical reaction leads to clearly visible colour changes with no apparent surface damage. This is achieved by adding pigments to the thermoplastic elastomer (TPE) substrate material.

Preferably the thermoplastic elastomer is injection mouldable. The thermoplastic elastomer may be a Kraton™-based polymer and the pigment additive may be TiO_2.

Preferably the pigment additive comprises 0.5 – 5.0% by weight of the material. Most advantageously for applications which require back lighting the pigment additive comprises 1.5% by weight of the material.

The material may further comprise up to 5% by weight of a thermoplastic polymer to enhance the mechanical and/or thermal properties of the material.

Preferably the absorption band of the pigment lies in the invisible band of the e.m. spectrum and in particular the UV band.

According to the invention there is also provided a method of marking a thermoplastic elastomer material, said material comprising a thermoplastic elastomer and a pigment additive, the pigment additive having an absorption band within a band of e.m. radiation which results in a photo-chemical

reaction when the material is subjected to e.m radiation in the absorption band, the method comprising:

subjecting the material to a laser beam having a wavelength of radiation in the absorption band such that the pigment undergoes a photo-chemical reaction.

Preferably the wavelength of radiation of the laser beam is in the range 300-400 nm, and most advantageously in the range 350-360 nm. The laser beam may be provided by a pulsed third harmonic YAG laser.

According to a third aspect of the invention there is also provided a method of making a laser-markable material, the method comprising:

adding pigment additive to a thermoplastic elastomer, said pigment additive having an absorption band in a band of e.m. radiation which results in a photo-chemical reaction taking place when the material is subjected to e.m. radiation in the absorption band,

mixing the pigment additive and the thermoplastic elastomer,

melting the mixed pigment additive and thermoplastic elastomer to form a molten material and forming the molten material into pellets or the like.

The invention also extends to an article made from the material according to the invention and in particular to keymats for use with portable devices such as radio telephones, personal digital assistants (PDAs), portable computers, palm tops, lap tops and the like.

According to a further aspect of the invention there is provided a laser-markable material, the material comprising a thermoplastic elastomer and 0.5-5.0% by weight of TiO_2. Preferably the material contains 1.5% by weight of TiO_2.

Such a material has been found to be particular suitable for keymats for portable devices such as mobile phones. The material can be injection mouldable, which is a significant improvement over silicon rubber which has to be compression moulded.

The material and manufacturing process according to the invention uses a thermoplastic elastomer as the raw material. The thermoplastic material is preferably injection-mouldable. The laser marking process is used for marking of texts and graphics.

The invention also allows the use of an automated inspection system for quantitative evaluation of laser-marked keymats.

The developed manufacturing process is expected to have the following advantages over the current process: TPE materials are recyclable economically; the production cycle time is reduced from around 65 minutes to 1 minute; component cost can be reduced by 25%; and high flexibility in customisation of a component is possible since the laser marking process is programmable. Additionally the resulting method is less labour intensive due to automation. The quality of resulting articles is also more consistent compared with known techniques.

The new laser marking technique uses a photo-chemical process, hereinafter referred to as laser colour-change marking. The characteristics of the laser colour-change marking include: no or minimal thermal effects; no or minimal surface material removal; no or minimal surface structural changes; and good marking contrast due to colour changes.

In order to achieve the colour-change marking, laser sensitive pigments are incorporated into the substrate materials. Under an appropriate laser

wavelength, pulse energy and peak power, a photo-chemically induced colour change occurs.

Thermoplastic elastomers (TPEs) are considered to be the most suitable thermoplastic material to be used. TPEs can be injection-moulded which is more productive than the compression moulding process used for silicon rubber keymats.

Laser marking contrast is an important quality criteria. Apart from the laser parameters, the types of pigments and their weight percentage ratios in the substrate materials play a major role in achieving adequate marking contrast. In general, higher pigment contents will lead to high laser marking contrast.

Translucency is another important quality criteria. The keymat must be sufficiently translucent to allow back-lights to transmit through so that texts and graphics can be seen in a dark environment. In general, lower pigment contents will lead to higher translucency. Commercial TPEs have different grades of translucency. This is one of the selection criteria of TPEs.

The contradictory effects of pigments on the laser marking contrast and on the keymat translucency require a compromised solution. The aim is to achieve the highest contrast with sufficient translucency.

The invention will now be described, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 shows an example of laser positive marking;

Figure 2 shows an example of laser reverse marking;

Figure 3 shows an example of an arrangement for laser mask marking;

Figure 4 shows an example of an arrangement for laser beam marking;

Figure 5 shows the parameters of a focussed laser beam.

In laser positive marking, a laser beam directly writes the texts or graphics on a material surface. In this description, the term "marking" refers to "positive marking" unless otherwise stated. Figure 1 shows a substrate forming a keymat 2 for a portable device such as a mobile telephone. As shown on Figure 1, in laser positive marking graphics and text 4 are produced by photo-chemical reaction of the substrate in the areas representing the graphics/text.

In laser reverse marking, a laser beam writes over the surrounding areas of texts or graphics. Figure 2 shows a substrate forming a keymat 2 for a portable device such as a mobile telephone. As shown on Figure 2, in laser reverse marking a colour change is produced in the areas 6 surrounding the desired graphics and text 4 by photo-chemical reaction of the substrate in these areas 6. Thus the buttons of the keypad are highlighted.

There are two basic methods for laser marking: mask marking and beam scanning marking. As can be seen in Figure 3, in mask marking a mask 30 showing the desired texts and graphics is positioned above the sample 32 of material. A lens 34 is provided to focus the laser beam 36. The laser beam transmits through the mask 30 and the lens 34 and an image 38 of the mask pattern 34 is produced on the sample surface.

Alternatively laser beam scanning marking may be used, in which a laser beams write directly on the surface of a sample of material. Figure 4 shows an exemplary arrangement for laser beam scanning marking. The movement of the laser beams 46 are controlled through two beam scanners 40, 41. Beam scanner 40 controls movement in the x-axis and beam scanner 41 controls movement in the y-axis. A lens focuses the controlled laser beams 46.

Mask marking is more suitable for high volume production with a fixed mask pattern, whereas beam scanning marking is more flexible in terms of pattern selection and size control.

Three major types of lasers are used in laser marking: CO_2, Nd:YAG & excimer lasers. As both of the CO_2 and Nd:YAG lasers have their wavelengths in the infrared range, the marking process by these lasers is conventionally a thermal process. However, the Nd:YAG laser can be frequency-tripled to achieve a wavelength of 355nm in the ultra-violet range. A KrF excimer laser has a wavelength of 248nm in the deep UV range. These UV lasers generate photo-chemical reactions and thus have minimum thermal effects on substrate materials.

Laser marking contrast is achieved through colour change in the material. The marking contrast is a function of many parameters, which include laser parameters (e.g., laser wavelength, pulse duration, peak power), material composition (e.g. pigments) and properties, and interaction parameters (such as marking speed and overlap).

Pigments are chemical compounds widely used for colouring plastics. White pigments achieve a white appearance by reflecting all wavelengths of light equally. Black pigments absorb all wavelengths equally. On the other hand, a specific coloured pigment imparts a desired colour by selectively absorbing and reflecting different wavelengths of the visible light spectrum. In selection of a pigment, the following characteristics should be considered.

- Colour
- Tinting strength (the ability of whitening a base material)
- Light fastness (UV resistance)
- Absorption band
- Opacity (a function of particle size and refractive index)

- Chemical reactivity (reaction with air pollutants may cause discoloration.)
- Thermal stability

The pigment titanium dioxide TiO_2 is colourless and appears white in powdered form. No absorption bands are present in the visible region for crystalline TiO_2. TiO_2 has a strong absorption band in the near UV band (below 400 nm).

Transition metal complexes (e.g. cobalt compound, iron compound, copper compound, lead compound, TiO_2) are particularly suitable for use as pigment additives to blend directly with thermoplastics. A suitable proportion of pigments (by weight) is from 0.5 - 5%.

Thus a material according to the invention is provided by pre-mixing in a closed chamber the powdered pigment with the thermoplastic polymer granules. The pre-mixed material is then melt compounded in a twin screw extruder and extruded as pellets for subsequent injection moulding applications.

To produce components from the material the pellets are heated and injected into moulds, in a conventional manner. The description makes particular reference to keymats for portable devices. However the material has many other uses.

The laser beam directed at the material has a bandwidth in the region of the absorption band of the pigment. The lasers used produce a photo-chemical reaction in the material and may be an infrared laser (in which a harmonic in the UV band may be used) or a laser the output of which is in the UV band. When a white or light-coloured substrate is used, use is made of a pigment

which becomes dark after undergoing a photo-chemical reaction so that the laser-induced marks are dark against the substrate.

The preferred pulse duration is 1-10 ns. This short pulse duration leads to high peak power, which induces photo-chemical reactions. This short pulse duration also reduces the thermal/heat transfer to surrounding materials and thus leads to minimal thermal effect.

For UV lasers such as excimer lasers and the third harmonic YAG laser, the colour change is primarily due to photo-chemical reactions with no or minimal material removal.

A specific example of the material and the laser used to mark the material will now be described.

- TPE material

Material	Supplier	Hardness
95% Dynaflex G2755 + 5% Polypropylene	GLS Corporation	Shore A +/- 65

A Kraton™-based thermoplastic elastomer has been selected and tested as a potential keymat material to replace silicon rubber. Kraton™ is the trade name for a series of thermoplastic elastomer materials manufactured by Shell Chemicals.

5% by weight of polypropylene is added to increase the hardness and mechanical and thermal properties of the resulting material.

- Pigment

The pigment selected is a surface-treated, ultrafine rutile titanium dioxide. It is organically coated to achieve fast and complete dispersion into various plastics. The major properties are listed in the table below:

Appearance	Odourless, white powder
TiO_2 content	Min. 90%
Modifiers, compounds	Alumina, Stearic Acid
pH	6-8
Specific surface area	50-70 m^2/g
Crystal size	17 nm

Pigment loading was 1.5% by weight.

- Cycle time

Injection moulding: 40 seconds

Laser positive marking: 1 minute

Laser for reverse marking: 11 minutes

- Laser marking system and key process parameters (see Figure 5)

The following definitions apply:

Laser pulse duration: lifetime of a laser pulse.

Laser peak power: maximum power of a laser pulse.

Focal spot size: the smallest laser beam diameter after a focusing lens

Depth of focus: the distance where the focal spot size is constant

Pulse repetition rate: number of laser pulses emitted per second.

Laser type	Pulsed 3rd harmonic YAG laser (355 nm)
Laser pulse duration	3 ns
Laser avg. power	0.8 W
Beam energy density on workpiece	21 J/cm^2
Pulse repetition rate	100 Hz

Beam scanning optics	Focal length: 180mm Scanning field: 99×99mm Working distance: 210mm Beam expansion: 2×
Marking speed	7mm/sec (0.07mm×100Hz)
Positioning speed	3m/sec
Marking software	Window based, AutoCAD file acceptable, barcode 39

The TPE material is economically recyclable. Keymats made by recycled TPEs have shown the same laser marking contrast as the original keymats.

The majority of the material properties of the selected TPE are comparable to those of silicon rubber except the keymat wearability. It is recommended that an overcoat is applied to enhance the wearability of the material, as is the case with conventional silicon rubber keymats.

An inorganic pigment, rutile TiO_2, has been chosen and tested for enhancing the laser marking contrast. The optimised loading is 1.5% in weight percentage, which gives good marking contrast and adequate translucency.

A pulsed 3rd harmonic YAG laser with a wavelength of 355 nm, together with a beam scanning unit has been developed to produce texts and graphics on the keymats.

Excellent laser marking contrast and resolutions are achieved. There is little thermal damage on the TPE surface. The marking depth is in the range of 50-100 μm. This developed process is thus called "volume" marking as compared to "surface" marking produced by the conventional laser marking techniques.

The laser marks are durable and not affected by solar radiation, temperature and humidity when subjected to cycle tests.

The Cpk values for all the relevant parameters of the laser marks are good (higher than 1.35-2.63), which indicate that the laser marking process is reliable and produces consistent results. The process yield by visual inspection is 100%.

A new manufacturing process involving both injection moulding and laser marking technologies for applications in mobile phones industry has been developed. The high Cpk values for both the injection moulding process and the laser marking process indicate that the developed process can be applied to the production floor.

The new material and process are more productive and more economical compared with existing silicon rubber techniques. The low keymat material cost and low operating cost will lead to significant cost reduction. Recycling of the TPE materials will further reduce the material cost.

Quantitative analysis of the laser marks is a great improvement over the conventional subjective visual inspection technique.

A second harmonic YAG laser has also been found to result in a photo-chemical reaction although the results are not as satisfactory as using a higher frequency laser.

CLAIMS

1. A material comprising a thermoplastic elastomer and a pigment additive, the pigment additive having an absorption band in a band of e.m. radiation which results in a photo-chemical reaction taking place when the material is subjected to a beam of e.m. radiation in the absorption band.

2, A material according to claim 1 in which the thermoplastic elastomer is injection mouldable.

3. A material according to claim 1 or 2, wherein the pigment additive is TiO_2.

4. A material according to claim 1, 2 or 3 wherein the pigment additive comprises 0.5 – 5.0% by weight of the material.

5. A material according to claim 4 wherein the pigment additive comprises 1.5% by weight of the material.

6. A material according to any preceding claim wherein the material further comprises up to 5% by weight of a thermoplastic polymer.

7. A material according to any preceding claim wherein the absorption band of the pigment lies in the UV band of e.m. radiation.

8. A method of marking a thermoplastic elastomer material, said material comprising a thermoplastic elastomer and a pigment additive, the pigment additive having an absorption band within a band of e.m. radiation which results in a photo-chemical reaction when the material is subjected to e.m radiation in the absorption band, the method comprising:

subjecting the material to a laser beam having a wavelength of radiation in the absorption band such that the pigment undergoes a photo-chemical reaction.

9. A method according to claim 8 wherein the wavelength of radiation of the laser beam is in the range 300-400 nm.

10. A method according to claim 8 wherein the wavelength of radiation of the laser beam is in the range 350-360 nm.

11. A method according to claim 8 wherein the laser beam is provided by a pulsed third harmonic YAG laser.

12. A method according to any of claims 8 to 11 wherein the laser beam pulse duration is from 1 to 10 ns.

13. A method of making a laser-markable material, the method comprising:

adding 0.5% to 5.0% by weight of pigment additive to a thermoplastic elastomer, said pigment additive having an absorption band in a band of e.m. radiation which results in a photo-chemical reaction taking place when the material is subjected to e.m. radiation in the absorption band,

mixing the pigment additive and the TPE,

melting the mixed pigment additive and TPE to form a molten material and forming the molten material into pellets or the like.

14. An article made from the material according to claims 1 to 7.

15. A keypad made from the material according to claims 1 to 7.

16. A radio telephone incorporating an article made from the material according to claims 1 to 7.

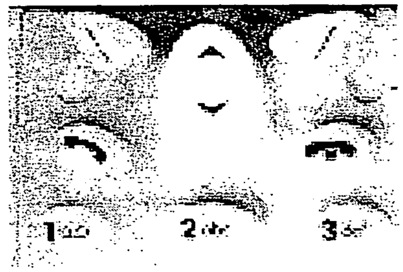

FIG. 1

LASER POSITIVE MARKING

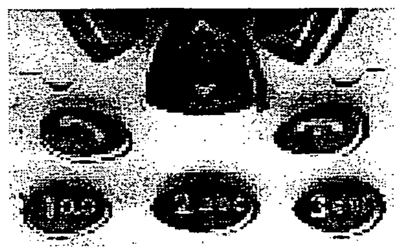

FIG. 2

LASER REVERSE MARKING

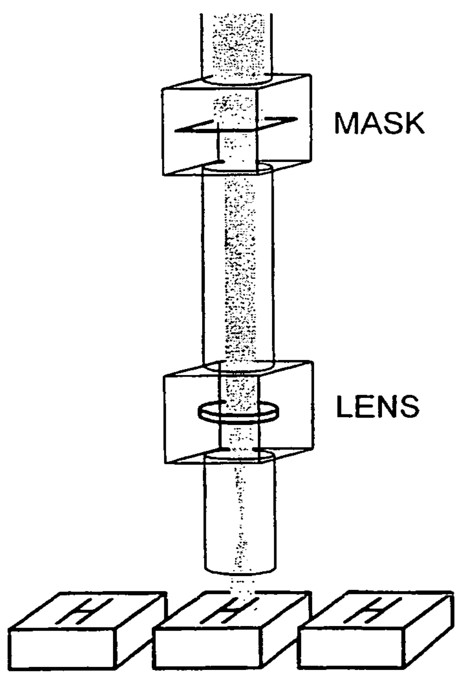

FIG. 3

SET-UP FOR LASER MASK MARKING

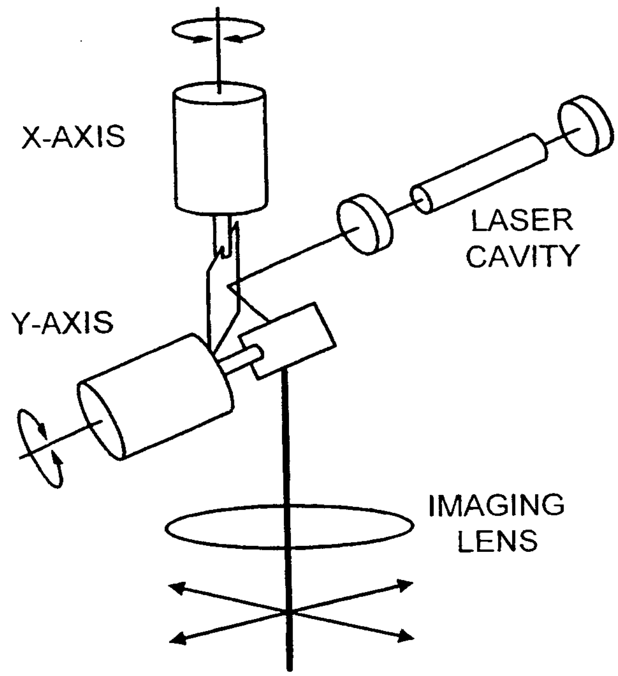

FIG. 4

SET-UP FOR LASER BEAM SCANNING MARKING

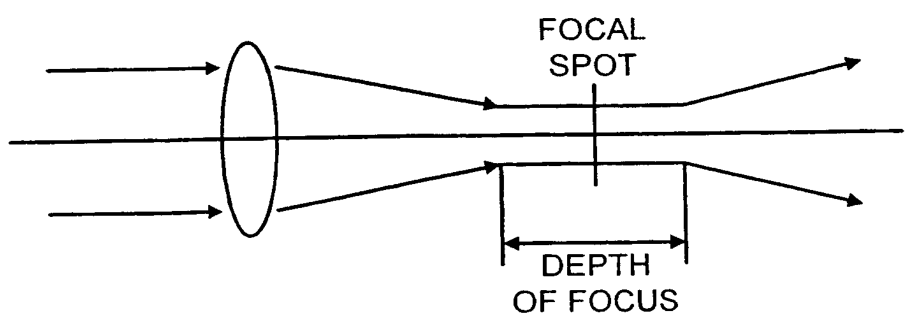

FIG. 5

SCHEMATIC OF A FOCUSED LASER BEAM

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08K3/00 B41M5/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08K B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 198621 Derwent Publications Ltd., London, GB; Class A18, AN 1986-134845 XP002152620 & JP 61 072049 A (NIPPON ELASTOMER KK), 14 April 1986 (1986-04-14) abstract ---	1-4,7
X	EP 0 400 305 A (HUELS CHEMISCHE WERKE AG) 5 December 1990 (1990-12-05) column 3, line 23 - line 40 example 4 claims 1-6 ---	1-16
X	EP 0 447 032 A (BRITISH AEROSPACE) 18 September 1991 (1991-09-18) claims 1-7 --- -/--	1-16

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
7 December 2000	20/12/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Siemens, T

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 550 032 A (HOECHST AG) 7 July 1993 (1993-07-07) claims 1-10 ---	1-16
X	DATABASE WPI Section Ch, Week 199914 Derwent Publications Ltd., London, GB; Class A35, AN 1999-162374 XP002152621 & JP 11 020316 A (NOK CORP), 26 January 1999 (1999-01-26) abstract -----	1-16

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern .al Application No
PCT/EP 00/07304

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 61072049 A	14-04-1986	NONE	
EP 0400305 A	05-12-1990	DE 3917294 A	29-11-1990
		AT 140189 T	15-07-1996
		BR 9002465 A	13-08-1991
		CA 2017545 A	27-11-1990
		DE 59010410 D	14-08-1996
		ES 2088917 T	01-10-1996
		JP 2947878 B	13-09-1999
		JP 3024161 A	01-02-1991
		KR 162082 B	15-01-1999
		US 5053440 A	01-10-1991
EP 0447032 A	18-09-1991	CA 2036765 A	16-09-1991
		JP 6093207 A	05-04-1994
		US 5206280 A	27-04-1993
EP 0550032 A	07-07-1993	DE 4143258 A	01-07-1993
		BR 9205192 A	06-07-1993
		CA 2086023 A	01-07-1993
		JP 5247319 A	24-09-1993
		MX 9207672 A	31-05-1994
JP 11020316 A	26-01-1999	NONE	